SOME FACTORS AFFECTING THE SOLUBILITY OF COBALT

by

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INTRODUCTION

In recent years it has been found that the element cobalt is essential for proper nutrition of ruminants. Consequently its uptake from the soil by pasture and crop plants has become of interest not only to animal husbandmen but to agronomists as well. There exists a considerable amount of literature dealing with the treatment of animals affected with cobalt deficiency by drenching, supplements in feeds, and the use of top dressings on deficient pastures. Some work has been done trying to correlate cobalt deficient pastures with parent material of the soil. However, the literature contains very little information pertaining to soil factors that affect the solubility and availability of cobalt. It was felt that information on this subject would be of considerable value to those interested in combating the "wasting disease" of ruminants caused by the lack of cobalt in their diet.

With this in mind, experiments were designed to determine the effect of hydrogen ion concentration and various cations and anions on the solubility of cobalt in solutions and to study the effect of anion and hydrogen ion concentration on the extraction of cobalt from soil.

REVIEW OF LITERATURE

A review of the literature revealed that the importance of cobalt in livestock nutrition and agronomy was not realized until recent years. According to Becker et al. (8) the "wasting disease" was known in Florida as early as 1888 where it was attributed to hookworms. It was corrected by using a mineral supplement, which in all probability contained some cobalt. In later years in Australia and New Zealand, the deficiency was attributed to a lack of iron, and was counteracted by an amendment of limonite, later found to contain cobalt. In 1934 Filmer and Underwood (12) attributed the deficiency to cobalt. Since then, in every case where ruminants were affected, a drench or supplement of cobalt has cured their affliction.

The deficiency of cobalt is rather widespread, having been reported in New Zealand by Kidson (16), McKnaught (21), Askew and Dixon (5), and others; in Australia by Harvey (15), Underwood and Filmer (35), and others; in Florida by Becker et al. (8); in New Hampshire by Lyford et al. (20); in Michigan by Killham (19) and in northeast Wisconsin by Geyer et al. (13).

Cobalt may give some stimulation, but is not considered essential for plant growth and is toxic except in very small quantities. Young (37) reported that cobalt was injurious to timothy and algae, that maize and barley were stimulated, and that wheat, rye, oats, beans and peas were uninjured by very small quantities of cobalt. Brenchley (9) used a nutrient solution and found that cobalt in concentration of E/64 was toxic to barley at pH 5 and completely checked growth at a concentration of E/16, where E is a solution containing the atomic weight of an element in milligrams per liter. Scharrer and Schropp (31) reported that cobalt sulfate was toxic except in small amounts but that some stimulation of root growth was obtained at small concentrations.

Investigators have reported wide variations in cobalt content of soils. A large number of samples analyzed in New Zealand by Kidson (16), who used a concentrated hydrochloric acid extract, contained from 0.3 to 380 p.p.m. Harvey (15) reported that some west Australian soils contained from less than 1 to more than 10 p.p.m. cobalt. Young (37) found from 0.26 to 11.7 mgms. per kilogram. Slater et al. (32), using a gravimetric method of analysis, found no cobalt in Keith, 0.2 p.p.m. in Colby silt loam, and from 0.9 to 2.4 p.p.m. in Marshall silt loam (Iowa).

Attempts have been made to correlate deficiencies of cobalt as shown by sickness of grazing animals with amounts obtained by chemical analysis of soil and herbage extracts. Kidson (16) found that sickness of animals is usually associated with soils having less than 2 p.p.m. cobalt, but did not consider a chemical estimation as sufficient criteria for recommendations regarding use of cobalt supplements. The same investigator (17) reported that sheep grazing on soils containing 3-4 p.p.m. cobalt were diseased whereas those on soils containing 11-30 p.p.m. cobalt were healthy. Becker et al. (8), using spectrographic estimation of cobalt in soil, concluded that 0.02 p.p.m. was the dividing line between "sick" and "healthy" soils. Patterson (29) found 3.9 p.p.m. cobalt in deficient soils and 16.7 in those that supported healthy sheep. He considered 0.2 p.p.m. as an adequate amount in the pasture plants. Corner and Smith (11) deemed 0.07 p.p.m. cobalt as sufficient in pastures. They found no correlation between soil and herbage content. Mitchell (27) considered 0.08

p.p.m. adequate in pasture plants and 0.04 p.p.m. as definitely low. Most investigators have extracted cobalt from the soil with concentrated hydrochloric acid. Mitchell (27), however, used acetic acid (pH 2.5) and considered 0.3 p.p.m. as sufficient and less than 0.25 p.p.m. as low. Kidson (16) stated that the use of N and N/10 hydrochloric acid made no difference in the relative amounts of cobalt extracted.

Various factors that affect the uptake of cobalt by plants have been reported. Among these are season of the year, lime content of the soil, moisture content, cobalt content (top dressings), parent material, species of pasture plant, soil type, stage of growth of plant, adsorption, and state of oxidation.

Askew and Maunsell (6) reported that the cobalt content of pastures was high in spring, fairly constant during summer and low in fall. They also noted that there is a sudden drop in the uptake of cobalt by pastures at the end of the growing season. McKnaught and Paul (24) found that pastures increased in cobalt content in late autumn and winter and decreased during spring and summer.

Mitchell (26) stated that large amounts of calcium carbonate in soil prevented absorption, and Askew and Maunsell (6) stated that applications of lime decreased uptake by plants. Stanton (33) found that a high carbonate content usually accompanied low cobalt content but that there was no correlation. Askew and Dixon (5) in pot experiments to which were added cobaltous chloride, cobaltous chloride plus superphosphate, and cobaltous chloride plus lime in varying amounts on different plants found that all were toxic except the cobaltous chloride plus lime. They also reported that lime gave a depressing effect on plant uptake of cobalt, especially where mixed before application. A limestone containing five p.p.m. cobalt, when applied at the rate of two tons per acre was reported by Askew (4) to have resulted in a small increase in cobalt content of pastures. The increase, however, was attributed to the cobalt contained in the lime and not to the lime releasing cobalt from the soil reserves.

It has been previously mentioned that usually soil high in cobalt resulted in herbage of high content, but that no good correlation existed. Top dressings of cobalt, however, have given increased cobalt content of plants. Mitchell (27) found a top dressing to be effective for three years. Its effectiveness was less persistent on a limed soil. Askew and Maunsell (6) reported that top dressings gave high cobalt content in plants at first, was maintained at medium amounts for quite a time, and then dropped rapidly near the end of the growing season. Askew and Dixon (5) stated that top dressings greatly increased cobalt content of pastures, and that cobalt mixed with superphosphate was a suitable mixture for applying cobalt because of its ability to encourage high intake of this element.

McKnaught and Paul (24) found that the cobalt content of pastures increased under drought conditions. Stanton and Kidson (34) stated that it was probable that moisture relations of soils, stage of plant growth, and species of pasture plant all play a part in cobalt content of pastures. McKnaught and Paul (24) reported that mature growth and hay contained less cobalt than closely grazed pastures. Ahmad and McCollum (1) found more cobalt in leguminous seeds than in cereals.

That a strong correlation exists between cobalt deficiency and parent material was shown by Lyford et al. (20). Eighty-two per cent of the deficient soils studied were derived from granitic material. The deficiency was greater on granitic till or outwash than on till derived from gray mica schist or on mixed till derived from granite and brown rusty mica schist. Askew and Maunsell (6), Askew (3), and Stanton and Kidson (34) all reported that granite derived soils were low in cobalt. Mitchell (27) found that soils derived from basic igneous rocks or argillaceous sediments were higher in cobalt than those from sandstone, limestone, and acid igneous rocks. McKnaught (22) indicated a fair correlation between parent material and cobalt deficiencies, in that deficient soils were derived from pumice shower, acid rhyolic shower and highly leached soils from basic rock, whereas the "healthy" soils were derived from basaltic ash or grey mud composed of rhyolitic ash mixed with basalt. Ultra basic rocks resulted in soils high in cobalt. Kidson (16) stated that the cobalt content of soils in general is related to the magnesium content of the parent rock. Goldschmidt (14) reported the ionic radius of Co^{++} as 0.82 Å. and Fe^{++} as 0.83 Å. and suggested that isomorphous substitution is possible if ionic radii do not vary over 10 or 15 per cent, which would account for the fact that cobalt is associated primarily with the ultra basic rocks. In addition, Mitchell (27) listed the ionic radius of Mg^{++} as 0.78 Å. and stated "mineral lattice replacement of Mg^{++} and to some extent Fe^{++} by cobalt and nickel is the normal mode of occurrence". McKnaught (23) reported a case of cobalt deficiency on a limestone soil derived from a colluvial deposit from a hill which consisted of Pliocene mudstone and sandstone formations alternating with unconsolidated limestone and calcareous sandstone. Stanton (33) suggested that a limestone low in cobalt may on weathering result in a soil rich in cobalt. He found no correlation between geological age and cobalt content, but that the spread of values was greater in the younger formations, especially in the Tertiary class. Carroll (10) found that gneisses and schists resulted in low cobalt, while dolerites had a much higher content. She stated that the amount of cobalt in soil depends upon its presence in parent material, intensity of weathering, and resistance of parent rock to weathering.

Becker et al. (8) suggested a correlation between soil type and cobalt content. Lyford et al. (20) indicated that there may exist a relationship between texture of plow layer and deficiency, but if so it is not marked. They also found that the deficiency was as prevalent on gray brown podzols as on true podzols. Mitchell (27) found no accumulation of cobalt in the iron rich horizons or in "iron pans". In cultivated soils there was little variation throughout the profile. He also found that most of the cobalt is bound up in the crystal lattice of the minerals and that it is adsorptively bound and more firmly held than the usual exchangeable bases. Acetic acid extracts (pH 2.5) contained considerably more cobalt than ammonium acetate extracts (pH 7).

Askew et al. (7), in determining the feasibility of manufacturing and using cobaltized superphosphate fertilizer, studied the solubility of cobalt phosphate. When the cobalt content was less than 0.2 per cent, they found that at least 80 per cent of the cobalt in the superphosphate was water soluble. Cobalt in other phosphatic fertilizers was soluble unless the pH was above 6, at which point the solubility decreased rapidly. In the laboratory, the per cent of water soluble cobalt was usually above 90 per cent regardless of whether the cobalt was added as $CoCl_2 \cdot 6H_2O$, $Co(OH)_2$, Co_2O_3, or Cobaltite ($CoAs_2$). If the pH of a water suspension of a phosphatic fertilizer was above 8, the soluble cobalt was almost nil. They stated "It is not impossible that plants may be able to use cobalt which may appear by the chemical test to be available to only a low degree".

Askew (2), in a further study of effect of hydrogen ion concentration on solubility of commercial cobalt phosphate, reported that its solubility corresponds to 2.45 p.p.m. He also found that cobalt phosphate was readily soluble in aqueous solutions at pH 2, and that the variation of per cent solubility of cobalt in cobaltized superphosphate and phosphatic fertilizers corresponded closely above pH 3 with the percentage of phosphate present as $H_2PO_4^-$ ion. It was suggested that cobalt in the superphosphate may form the compounds $Co(H_2PO_4)_2$ and $CoHPO_4$, which are analagous to mono- and di- calcium phosphates respectively and exhibit similar solubility relationships in that $Co(H_2PO_4)_2$ is soluble in water, whereas $CoHPO_4$ is sparingly soluble. Since hydrogen ion concentration regulated the proportion of the various phosphate ions, it is to be expected that the solubility of cobalt in phosphatic fertilizers would show marked changes with pH values. Percentage of total cobalt that is soluble in water was reported as follows: 95.3 per cent at pH 2, 94.3 per cent at pH 4.5, 68 per cent at pH 6.1, 10.1 per cent at pH 7.4 and 0.03 per cent at pH 10.5.

Mellor (25, p. 567) stated that when potash-lye was added to cobaltous salts out of contact of air, a blue precipitate formed, which turned violet and then rose red. This precipitate can be detected in a solution of cobaltous nitrate containing one part cobalt per 80,000. An electrometric titration of a 0.0247 M solution of cobaltous chloride with 0.09 N sodium hydroxide at 18° C. started precipitating at pH 6.81. In the same publication (p. 586), he stated that cobaltic oxide is decomposed by most acids in the cold with the formation of the cobaltous salt. He also stated that it has been shown that cobaltic oxide decomposed in cold phosphoric, sulfuric, nitric, hydrochloric, and acetic acids. The decomposition with the acetic acid is slower than with the other acids. Goldschmidt (14) stated that the oxidation of cobalt may immobilize it.

PROCEDURES FOR THE DETERMINATION OF COBALT

Determination of Cobalt in Concentrated Solutions

The common colorimetric methods of determining cobalt are best suited to exceedingly dilute concentrations of this element.

Since many of the solutions being dealt with contained two per cent or more cobalt, it was deemed advisable to use a method that did not require such large dilutions as the above procedures, because of possible introduction of cobalt with the water and because inherent errors in determination would be greatly magnified. The existing literature for such a method was examined, but those found did not possess outstanding accuracy and were rather tedious. Since all of the cobalt solutions being used possessed a pink or red color, the feasibility of estimating cobalt colorimetrically by determining the absorption of light by the solution was studied, with the result that it was adopted for determining cobalt in pure solutions where the concentration of cobalt was above about 500 p.p.m. The initial work toward developing this procedure was devoted to solutions of cobaltous chloride.

A Coleman spectrophotometer, Model 11 was used for the determination of light absorption. A one centimeter round absorption cell was employed. Water was used as the reference blank. The wavelength of maximum absorption was determined to be 505 millimicrons (Table 1, Fig. 1). The solution obeyed Beer's law fairly well and determinations were valid over a range from about 0.05 per cent to at least 0.5 per cent cobalt. Sodium and potassium ions in the cobalt solution exerted little influence upon the absorption of light. Calcium, magnesium and ammonium ions increased the absorption of light a small amount as shown in Table 3, but it was felt that the influence was not of great enough magnitude to warrant corrections.

While this method was subject to errors caused from introduction of various ions and to the other errors inherent in colorimetry, it possessed the advantage of being very rapid. It exhibited greater accuracy than the Nitroso-R-salt method of determining cobalt to be described later. An undesirable feature of the method was that it is limited to relatively pure solutions. Time had no effect upon the absorption of light.

Table 1. Wavelength of maximum absorption of an aqueous solution of cobaltous chloride (1179 p.p.m. cobalt).

Wavelength	Transmission	$\frac{1}{T}$	Log $\frac{1}{T}$
Millimicrons	Per cent		
400	97.0	1.003	0.012
450	88.0	1.137	0.055
460	84.0	1.192	0.076
470	81.5	1.225	0.089
480	78.5	1.273	0.105
490	76.5	1.308	0.116
500	74.75	1.337	0.126
505	74.25	1.348	0.130
510	74.75	1.337	0.126
515	76.0	1.316	0.120
520	77.0	1.298	0.113
530	81.0	1.235	0.092
540	85.0	1.176	0.070
550	87.0	1.148	0.060
600	98.0	1.020	0.008
650	98.5	1.015	0.006
700	99.0	1.010	0.003

Subsequent work with cobaltous nitrate and sulfate solutions revealed that the method was equally applicable to these salts and that the absorption of light by them was approximately the same as with the chloride. These data are reported in Table 2. Slightly different wavelengths of maximum absorption were observed, however, with cobaltous nitrate exhibiting its maximum at 503 millimicrons and cobaltous sulfate at 499 millimicrons. This difference may well be within experimental error.

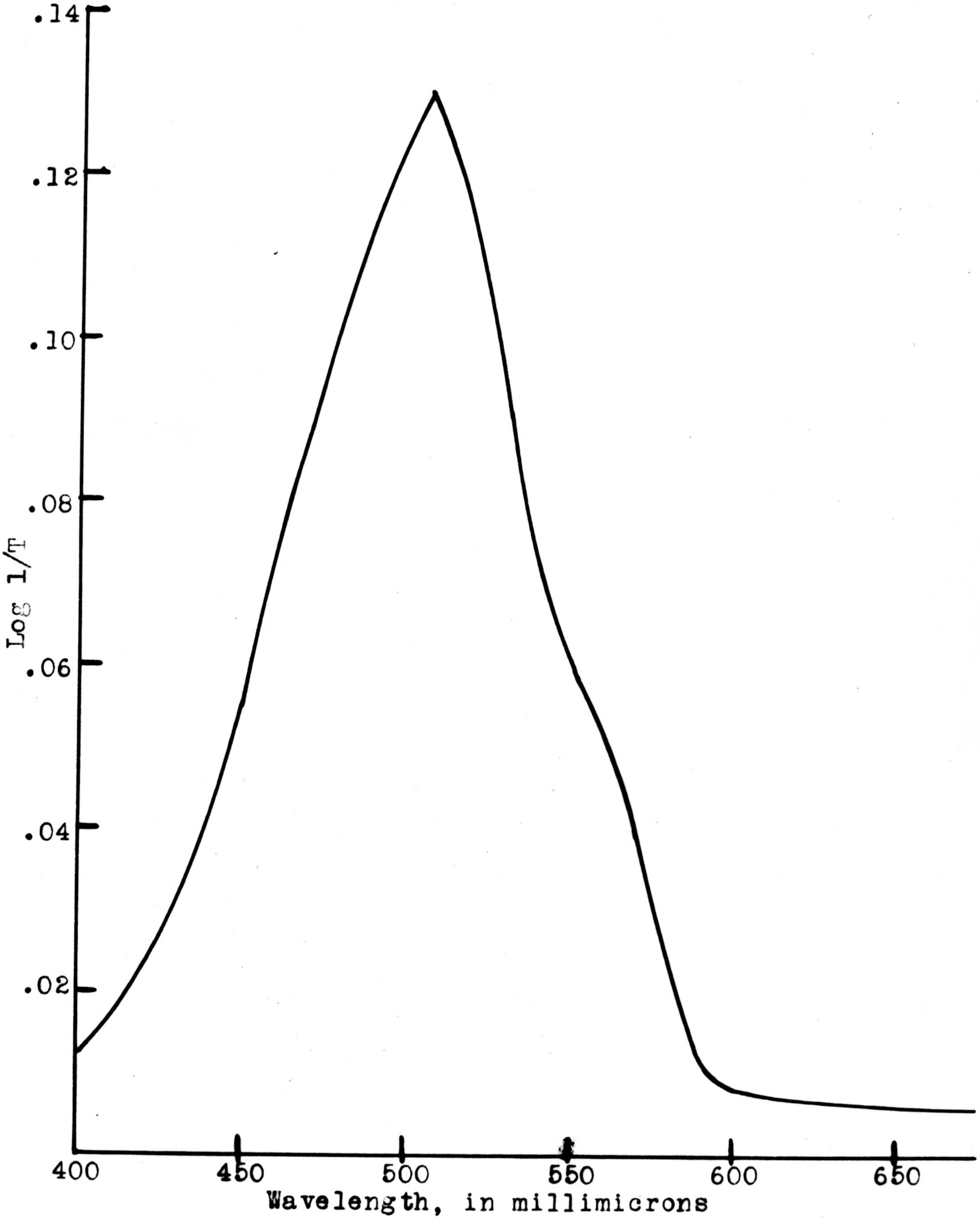

Fig. 1. Wavelength of maximum absorption by an aqueous solution of cobaltous chloride (1179 p.p.m. cobalt).

Table 2. Absorption of light by aqueous solutions of cobaltous salts.

Concentration of cobalt	Cobaltous chloride		Cobaltous nitrate		Cobaltous sulfate		Cobaltous acetate		Cobaltous phosphate	
	T	Log $\frac{1}{T}$	T	Log $\frac{1}{T}$	T	Log $\frac{1}{T}$	T	Log $\frac{1}{T}$	T	Log $\frac{1}{T}$
p.p.m.										
8841	11.5	0.940	---	---	---	---	---	---	---	---
5894	23.0	0.539	---	---	---	---	14.25	0.838	---	---
4710	32.0	0.495	32.5	0.488	32.0	0.495	21.5	0.688	41.0	0.388
2355	56.0	0.252	56.0	0.252	55.5	0.256	46.0	0.337	65.25	0.185
1884	63.0	0.201	62.5	0.204	62.5	0.204	54.0	0.267	70.5	0.152
1414	70.0	0.155	70.0	0.155	70.0	0.155	62.0	0.208	79.5	0.100
943	79.0	0.102	79.0	0.102	79.0	0.102	73.5	0.135	84.0	0.076
471	90.0	0.046	88.25	0.054	90.0	0.046	86.5	0.063	92.5	0.034
236	95.0	0.022	94.5	0.024	94.5	0.024	93.0	0.031	96.0	0.017
94	---	---	98.5	0.006	99.0	0.004	96.0	0.016	99.0	0.004

Cobaltous acetate, while its wavelength of maximum absorption (499 millimicrons) was about the same as those previously mentioned, exhibited much greater absorption of light by solutions of equal concentration (Table 2).

Cobaltous phosphate exhibited maximum absorption at 503 millimicrons. It absorbed less light than the previously mentioned solutions (Table 2).

Beer's law was obeyed by all of the above solutions, as shown in Fig. 2.

Table 3. Effect of cations on the transmission of light by cobaltous chloride.

Treatment*	Transmission (T)	Decrease in transmission	Cobalt concentration	Apparent increase in cobalt concentration
		Per cent		
Water	74.0	--	0.119	--
0.5N NaCl	74.0	0	0.119	0
0.5N KCl	73.75	0.3	0.120	1
0.5N $CaCl_2$	73.0	1.3	0.124	4
0.5N $MgCl_2$	73.25	1.0	0.123	3
0.5N NH_4Cl	73.0	1.3	0.124	4

* (5 ml. of 2 N cobaltous chloride plus 5 ml. of each reagent were made up to 250 ml.)

Determination of Cobalt in Dilute Solutions

While the above described method of estimating cobalt was valid on solutions containing over 500 p.p.m. cobalt, it could not be expected to give reliable results on exceedingly dilute solutions, because of the lack of coloration of dilute solutions, and consequently the low degree of light absorption. According to the literature

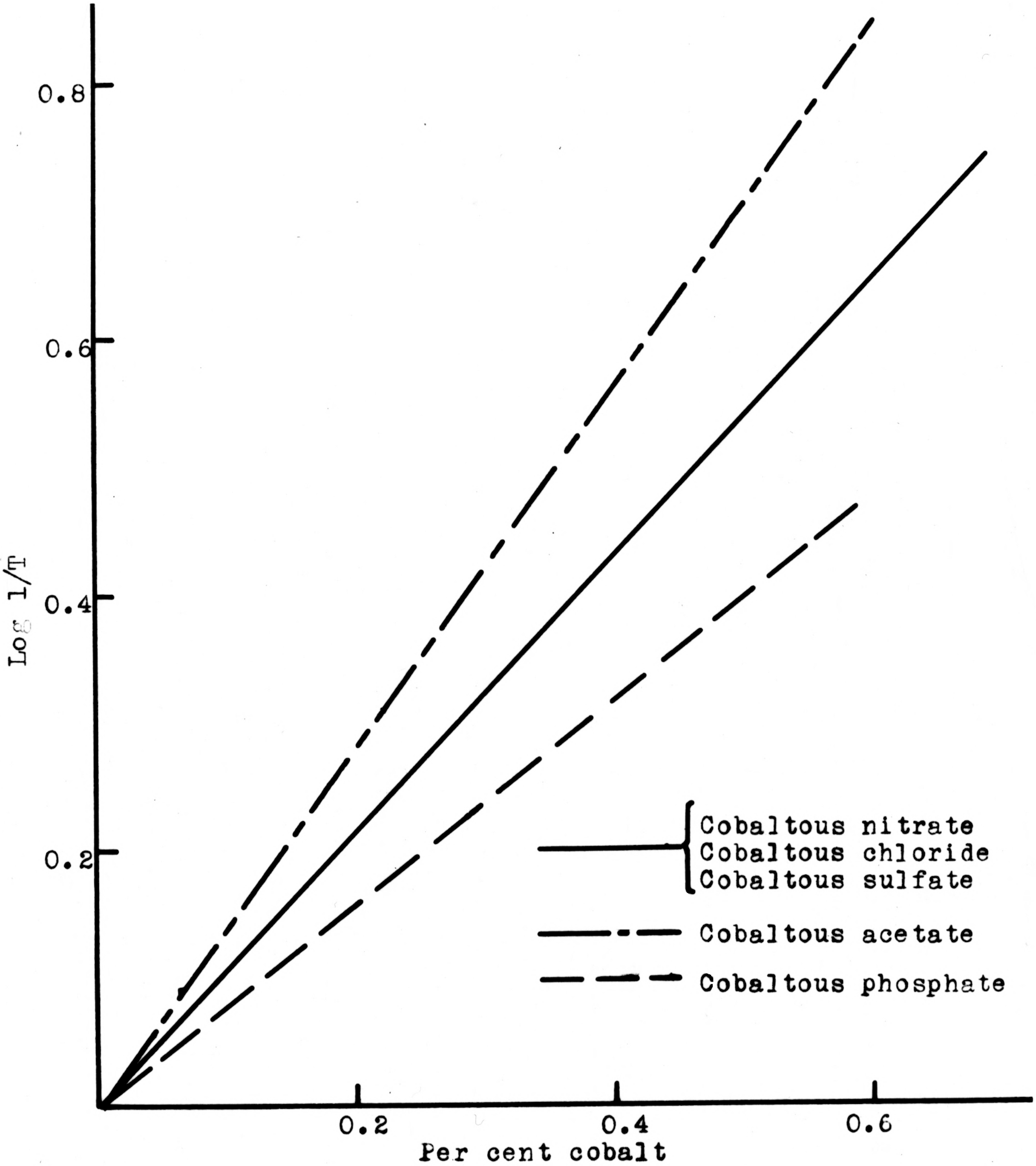

Fig. 2. Deviation from Beer's law exhibited by aqueous solutions of cobaltous salts.

reviewed, there are several compounds that give intense colors with cobalt. Nitroso-R-salt seemed to be best suited to the conditions of this experiment and was tested on standard solutions of cobalt using the modified procedure of Bayliss and Pickering as described by Piper (30).

The wavelength of maximum absorption was determined to be 420 millimicrons. This value did not check with the wavelength of 500 millimicrons used by Parks et al. (28) in determining cobalt by the method of Martson and Dewey, which is very similar to the one used here. They do not state that 500 millimicrons is the maximum; merely that it was the one used. It is evident from Fig. 3 that the absorption found was considerably more at 420 millimicrons than at 500 millimicrons. A recent publication by Willard and Kaufman (36) bears out the fact that maximum absorption occurs at 420 millimicrons.

Duplicate samples using the above method did not check within the desired limit. Literature on the Nitroso-R-salt method of color development revealed that certain investigators deemed it necessary to add the Nitroso-R-salt before neutralization (Kidson and Askew, 18), while McKnaught (21) held the opposite view. Kidson and Askew (18) used solid sodium acetate as a buffer and adjusted the pH of the mixture using phenolphthalein as the indicator, whereas Bayliss and Pickering recommended a solution of ammonium citrate buffered at pH 8.3 and no adjustment of pH. Various intensities and lengths of heating were also found to be used by various investigators. The effects of these factors were

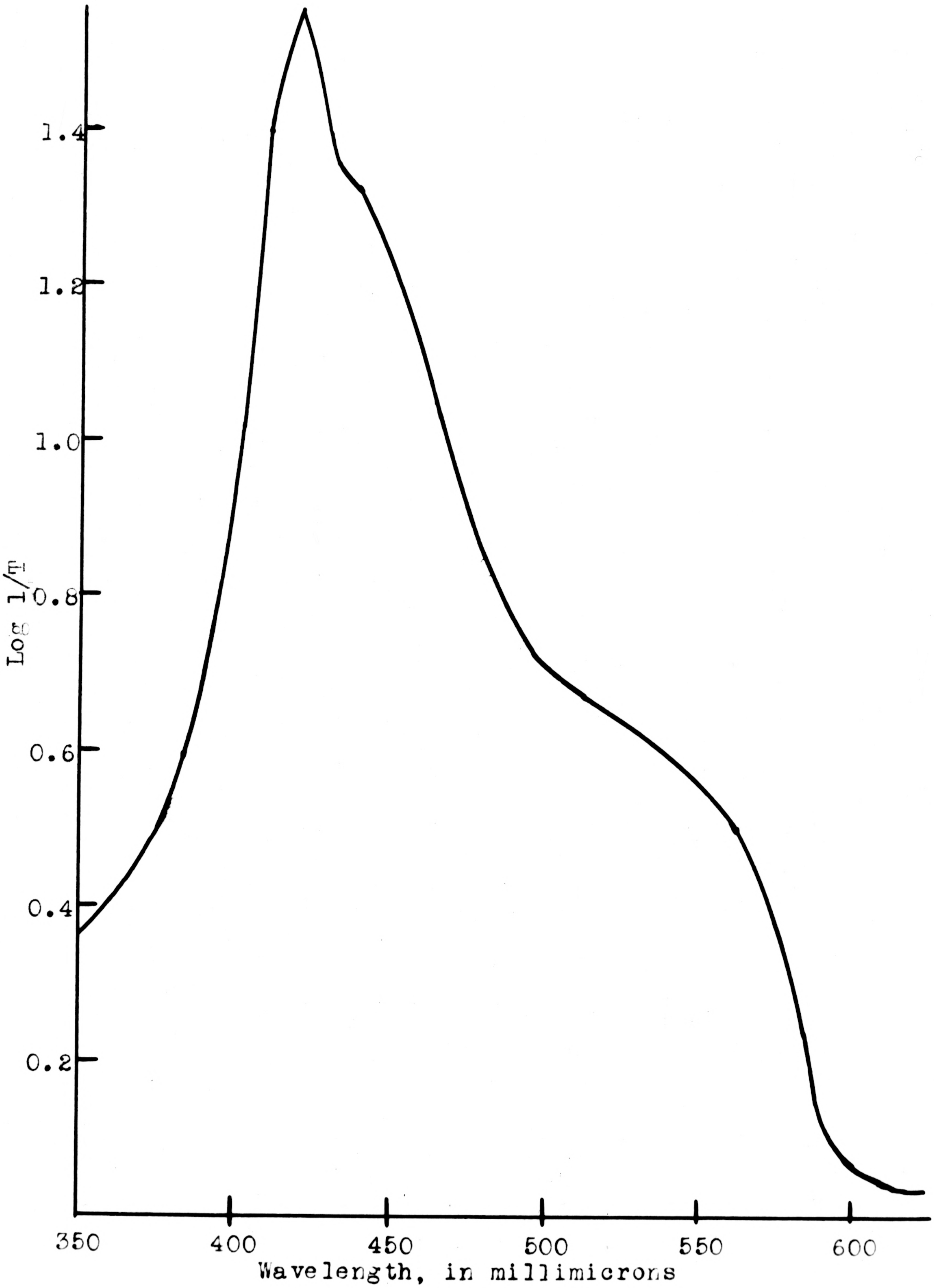

Fig. 3. Wavelength of maximum absorption by the cobalt complex of Nitroso-R-salt.

studied, with the conclusion that the maintenance of a pH value of about 8.3 during the initial boiling (precipitation of the cobalt-Nitroso-R-salt complex) and a constant intensity and length of heating were the critical factors. During two minutes of boiling, the mixture buffered with ammonium citrate increased in acidity from pH 8.3 to 5.7. A buffer of sodium borate was substituted and found to maintain the pH value during boiling. As a result, much better checks were obtained. The length of boiling was reduced to exactly one minute in each case, which also led to an increase in reproducibility of results (Table 4).

Table 4. Per cent transmission of duplicate samples of the cobalt-complex of Nitroso-R-salt using the method of color development outlined by Bayliss and Pickering as modified.

Sample number	Transmission 1	Transmission 2
	Per cent	
1	52.0	53.0
2	39.0	41.0
3	21.0	22.0
4	10.0	10.0
5	3.75	3.25
6	51.0	53.0
7	36.5	34.0
8	21.0	25.0
9	14.5	15.0
10	8.5	8.0

The exact procedure adopted was as follows:

Reagents:

Concentrated HNO_3

Sodium borate buffer
3.0918 gms. Boric acid
3.8276 gms. KCl
54 ml. 0.1838 N NaOH
Distilled water to make 1000 ml.
Adjust to pH 8.3-8.4

Nitroso-R-salt
1 gm. Nitroso-R-salt in 100 ml. distilled water

Bromine water, saturated

Standard cobalt solution
0.4037 gms. $CoCl_2 \cdot 6H_2O$
10 ml. con. HCl
Distilled water to make 1000 ml.
(One ml. contains 100 micrograms of cobalt)

Store all reagents in pyrex containers.

Procedure:

Pipette 5 ml. of cobalt solution containing from 1 to 4 p.p.m. cobalt into a 125 ml. pyrex erlenmeyer flask. Add 5 ml. of sodium borate buffer solution and 0.5 ml. Nitroso-R-salt reagent. Boil for exactly one minute, cool, add 5 ml. concentrated HNO_3, boil exactly one minute, remove, add 2.5 ml. saturated bromine water, digest for 10 minutes on a hot plate at 60-70° C., boil one minute to expel the bromine, cool, transfer to a graduated cylinder or test tube and make up to 15 ml. with distilled water. Compare in a spectrophotometer at a wavelength of 420 millimicrons. The reference blank is prepared exactly as the unknown except 5 ml. of distilled water is used instead of the cobalt solution. Several standards should be included in each run to check the working curve. In the event the cobalt solution is strongly acid, it should be neutralized before adding the buffer solution. This may be done by adding one drop of phenolphthalein (0.05 gms. in 100 ml. of 50 per cent ethyl alcohol) and titrating to a faint pink color with 10 per cent NaOH or KOH.

All reagents must be free from cobalt. They may be purified in most cases by distilling in an all pyrex still. No difficulty was experienced in this laboratory with the reagents or the water. Distilled water was obtained from an all aluminum still.

Time had little effect on the color of the complex as indicated by Table 5. Beer's law was obeyed between about 0.8 p.p.m. and 4.5 p.p.m. cobalt (Fig. 4), based on concentration of the original solution or between less than 0.3 p.p.m. to about 1.5 p.p.m. cobalt based on the solution actually placed in the spectrophotometer for comparison. Willard and Kaufman (36) reported that concentrations less than 2 x 10^{-4} mg./ml. or 0.2 p.p.m. did not hold to Beer's law.

Table 5. Effect of time on absorption of light by the cobalt Nitroso-R-salt complex.

Sample number	Transmission		
	Immediately	After 1 hour	After 45 hours
		Per cent	
1	52.0	52.0	53.0
2	20.0	20.0	22.5
3	3.5	3.5	4.0
4	5.0	5.0	6.0
5	50.0	50.0	52.0

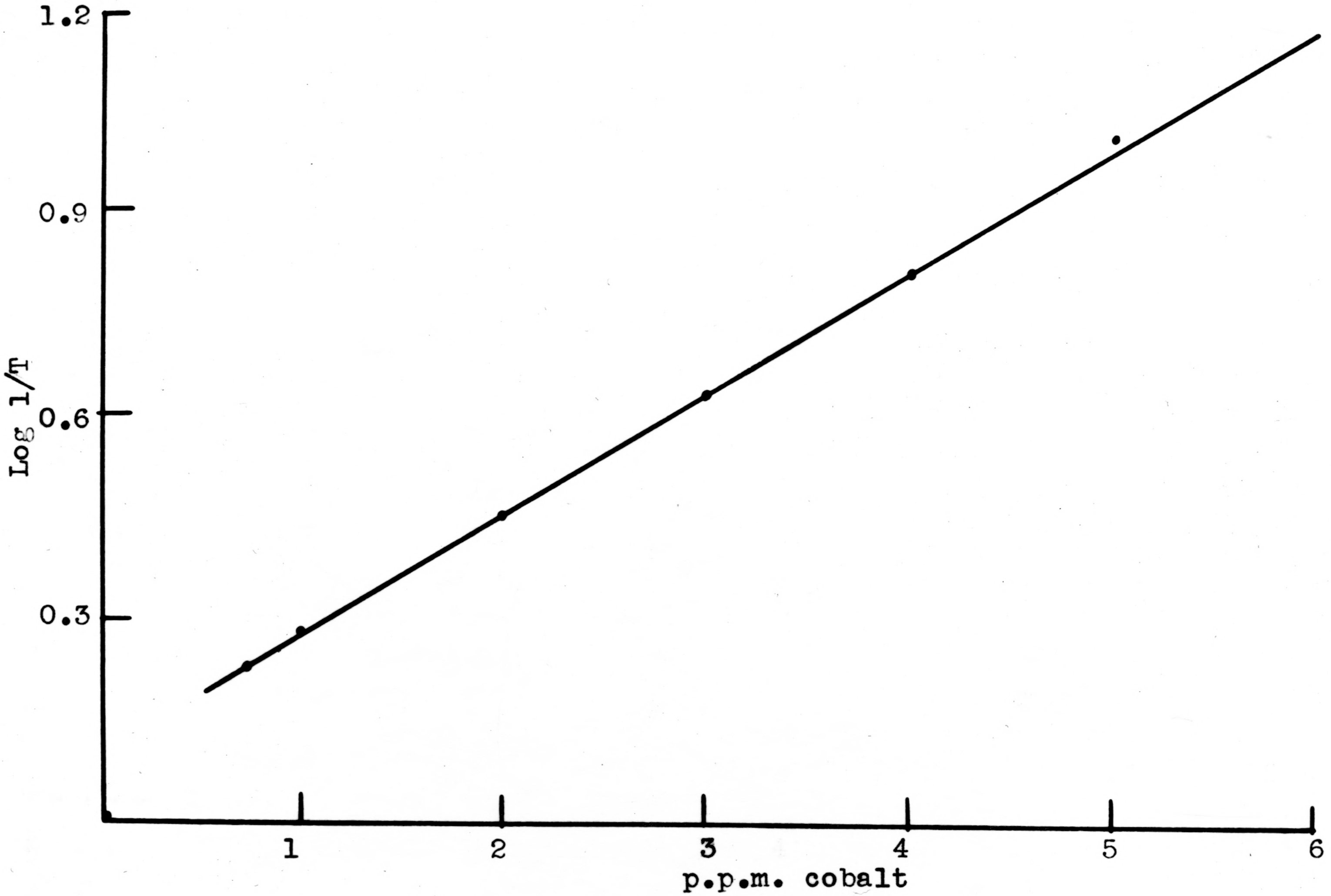

Fig. 4. Deviation from Beer's law (Cobalt complex of Nitroso-R-salt).

Determination of Cobalt in Soil Extracts

Soil extracts contain many ions, some of which interfere with the Nitroso-R-salt formation of color with cobalt, either by destroying the reagent, forming a color with the reagent, or by altering the final color. Consequently, these interfering ions must either be removed or rendered ineffective. McKnaught (21) reported that the presence of citric, oxalic, or nitric acid in the solution before neutralization resulted in partial to complete destruction of the Nitroso-R-salt reagent. Kidson and Askew (18), however, maintained that this was not the case, and added the reagent while the solution was in the acid condition. It can be assumed safely that strong oxidizing reagents will destroy the reagent, however. A slightly alkaline condition (pH 8-8.5) is necessary for the complete formation of the cobalt complex, but once formed, it is stable in strong nitric acid. The Nitroso-R-salt complex of most other metals is destroyed or at least partially so in hot strong nitric acid, which is the reason for adding nitric acid after the formation of the complex. McKnaught (21) indicated that peroxides will destroy the cobalt complex. He also reported that copper, if present in quantities larger than a trace, gave a green color, and that ammonium salts altered the final tint. The sulfates, chlorides, and phosphates of sodium, potassium, calcium, and magnesium made no alteration, while titanium, chromium and vanadium in small amounts had no effect on the final color. Nickel in concentrations 20 times that of cobalt did not interfere. He found, however, that iron gave an increase in color and had to be removed. The removal could not be effected by precipitation because of the occlusion of cobalt in the precipitate. Iron was removed by ether extraction in strong HCl as the covalent ether soluble ferric chloride. Kidson and Askew (18) found that quantities of iron, manganese and titanium present in pasture plants did not interfere. With soil extracts, iron should be removed, but no difficulty with other elements was experienced in the investigation reported in this paper.

The preliminary treatment of the soil extracts was carried out according to the following procedure:

Place 100 ml. of the clear extract (equivalent to 50 grams of soil) in a beaker and evaporate to dryness on a hot plate, add 2 ml. of concentrated H_2SO_4, transfer to a crucible, evaporate to dryness, ignite at dull red heat, take up with HCl (1:1), filter and make up to 100 ml. with HCl (1:1), take an aliquot containing from 5 to 20 micrograms of cobalt, extract with two volumes of ether in a separatory funnel, repeat if the aqueous phase still has a yellow tinge, place aqueous phase in a 125 ml. pyrex Erlenmeyer flask and evaporate just to dryness, add 5 ml. of distilled water, one drop of phenophthalein and adjust to a faint pink color with 10 per cent NaOH, add 5 ml. of sodium borate buffer and proceed to develop the color as prescribed for dilute solutions.

The accuracy of the method leaves much to be desired. Parks et al. (28) reported errors up to about 16 per cent. As indicated in Table 6, errors up to 35 per cent were found in the recovery of cobalt added to soil extracts. This is not too excessive, however, when consideration is given to the extremely small amounts of cobalt in soil extracts.

Table 6. Recovery by the Nitroso-R-salt method of cobalt added to soil extracts.

Sample number	Cobalt in extract	Cobalt added	Total cobalt determined	Cobalt recovered	Recovery of cobalt
	Micrograms				Per cent
1	12.7	5	17.2	4.5	90
2	16.0	5	22.0	6.0	120
3	0	5	3.25	3.25	65
4	2.0	5	8.5	6.5	130
5	1.9	5	8.3	6.4	128
6	0	5	3.25	3.25	65
7	0	5	4.75	4.75	95
8	0	5	5.0	5.0	100
Average per cent recovered					99.1

Determination of Total Cobalt in Soils

The following procedure was adopted for determination of total cobalt in soils:

Weigh 5 gms. of soil in a silica basin, ignite at dull red heat, cool, add 30 ml. concentrated HCl, warm, filter, and make up to 100 ml. with HCl (1:1). Take a 10 ml. aliquot, extract with ether and proceed as outlined above.

EXPERIMENTAL METHODS

Since the soil is so complex and the control of variable factors is so difficult, it was deemed advisable to use pure solutions in determining the effect of hydrogen ion concentration and various cation and anions on the solubility of cobalt. The effect of hydrogen ion concentration and anions on the extraction of cobalt from soil was investigated using a sample of Geary silty clay loam soil obtained from the Agronomy farm at Manhattan, Kansas. The experimental work was divided into three sections; the effect of hydrogen ion concentration and cations on the solubility of cobalt, the effect of hydrogen ion concentration and anions on the solubility of cobalt, and the effect of hydrogen ion concentration and anions on the extraction of cobalt from Geary silty clay loam soil.

Effect of Hydrogen Ion Concentration and Cations on the Solubility of Cobalt

Sodium, potassium, calcium, magnesium, and ammonium ions were selected as the cations. Cobaltous chloride hexahydrate was used as the source of cobalt, and the desired acidity was obtained by using hydrochloric acid. The desired alkalinity in each trial was obtained by adding proper amounts of the hydroxide or oxide of the particular cation being investigated.

The stock solution used was a 4 N solution of cobaltous chloride in 0.48 N hydrochloric acid. Ten ml. of this solution was added to each of 12 bottles with a capacity of 100 ml. Varying amounts of sodium hydroxide were added to 11 of these, resulting in a series of 12 samples with the first one containing no sodium and a pH of about 1, the last one containing 48.2 m.e. of sodium and having a pH of above 11, and the intermediate ones between these values both in amount of sodium and in reaction. The volume was made up to 50 ml. and the bottles tightly stoppered. They were shaken in an end over end shaker in a constant temperature room at 25° C. ± 1° C. for 21 hours, at which time they were removed and the pH determined with a Beckman pH meter. The samples were filtered and the cobalt estimated by the method described for concentrated solutions, except for the last two of the series which were analyzed by the Nitroso-R-salt method.

The above procedure was repeated using CaO, MgO, KOH, and NH_4OH in the place of NaOH. Each of the above series of experiments was conducted on different days. To be sure that daily conditions were not causing differences in results, a series of samples of all the cations was conducted at the same time (bottles 1 to 5 contained 7.14 m.e., 6 to 10 contained 20.07 m.e., and bottles 11 to 15 contained 37.5 m.e. of sodium, potassium, calcium, magnesium, and ammonium ions, respectively).

Effect of Hydrogen Ion Concentration and Anions on the Solubility of Cobalt

The chloride, nitrate, sulfate, acetate, and phosphate ions were selected as the anions in this investigation. Hydrogen ion concentration was adjusted with sodium hydroxide and the acid of the respective anion. The sources of cobalt used were the hydrated cobaltous salts of each anion.

Stock solutions of each were as follows: 4 N cobaltous chloride in 0.48 N hydrochloric acid, 4 N cobaltous nitrate in 0.49 N nitric acid, 2 N cobaltous sulfate in 0.2115 N sulfuric acid, both 1 N and 2 N cobaltous acetate in 0.24 N acetic acid, and saturated cobaltous phosphate in 0.21 N phosphoric acid. The reason for the different concentrations was due to the different solubilities exhibited by each salt.

Ten ml. of the stock solution of cobaltous chloride were pipetted into a series of 12 bottles. Sodium hydroxide in amounts varying from none to 48.2 m.e. was added to the series and the volume made up to 50 ml. After stoppering, they were shaken in an end over end shaker for 21 hours in a constant temperature room at 25° C. ± 1° C. At the end of this period, the pH of each was determined with a Beckman pH meter. After filtering, the cobalt content of the filtrate was estimated by the method described for concentrated solutions except the very dilute ones, which were analyzed by the Nitroso-R-salt method.

The above manipulations were repeated using the cobaltous nitrate stock solution instead of cobaltous chloride. Since the stock solutions of cobaltous sulfate and acetate were more dilute, 20 ml. of each were used, and the entire procedure repeated. Twenty ml. of cobaltous phosphates were used but since it was a very dilute solution, much less sodium hydroxide was added, varying from none to 5.5 m.e. throughout a series of 8 samples instead of the usual 12. Cobalt in the final solution was estimated by the Nitroso-R-salt method.

As with the cations, it was deemed advisable to complete a few samples of each anion at the same time so that there would be no doubt as to any effect resulting from changes in conditions from day to day. The phosphate, however, was omitted from this series because of the impossibility of obtaining strong solutions of cobaltous phosphate. Six samples of each; chloride, nitrate, sulfate and acetate, were carried to completion. The amounts of sodium added to each series varied from none to 46 m.e. Ten ml. of 4 N cobaltous chloride and cobaltous nitrate and 20 ml. of 2 N cobaltous sulfate and cobaltous acetate were used so that the resultant concentrations of cobalt were equal in each case.

Effect of Hydrogen Ion Concentration and Anions on the Extraction of Cobalt from Geary Silty Clay Loam

Extracting solutions investigated were as follows: 0.5 N sodium chloride, sodium nitrate, sodium sulfate, sodium acetate, and sodium phosphate adjusted or buffered at pH 6.7; each of the above adjusted or buffered at pH 5.8; 0.5 N hydrochloric acid, nitric acid, sulfuric acid, acetic acid, and phosphoric acid, 0.1842 N hydrochloric acid, 0.0921 N hydrochloric acid, 0.046 N hydrochloric acid, 0.0184 N hydrochloric acid, and 0.0074 N hydrochloric acid.

The method of obtaining the soil extracts was as follows: 125 gms. of Geary silty clay loam (pH 5.8) was passed through a 10 mesh screen and placed in centrifuge bottles of about 500 ml. capacity. Each of the above extracting solutions in the amount of

250 ml. was added. They were tightly stoppered and shaken in an end over end shaker in a constant temperature room at 25° C ± 1° C. for 14 hours. The samples were centrifuged and the supernatant liquid was siphoned off. Those that were not clear were filtered through clay filters. After determining the pH of the supernatant liquids, cobalt was estimated by the method outlined for soil extracts.

Total cobalt was also determined on the soil sample using the procedure described above for total cobalt.

EXPERIMENTAL RESULTS

The effect of hydrogen ion concentration cannot be entirely separated from the cation or anion influence because in each case it was necessary to include at least one of each for the purpose of adjusting pH. For this reason the results are divided into three parts; namely, the effect of hydrogen ion concentration and cations on the solubility of cobalt, the effect of hydrogen ion concentration and anions on the solubility of cobalt, and the effect of hydrogen ion concentration and anions upon the extraction of cobalt from soil.

The Effect of Hydrogen Ion Concentration and Cations on the Solubility of Cobalt

The data obtained are tabulated in Tables 7 and 8. Each operation toward obtaining the data presented in Table 8 was carried out at one time, thus excluding possible effects of any external variables such as variation in carbon dioxide content of the water, carbon dioxide pressure, errors in determining pH, etc. A graphical presentation of the results is shown in Figs. 5 and 6.

Hydrogen ion concentration had a pronounced effect on the solubility of cobalt. It was extremely soluble below about pH 6.5 Some precipitation may have begun at about pH 6.4, and in every case it had started at pH 6.61. Above this value, precipitation proceeded at a rapid rate with from 50 to 80 per cent being insoluble at pH 7.0. Almost total precipitation occurred at pH 8.5 or slightly above, except when the ammonium ion was present.

Table 7. The effect of hydrogen ion concentration and cations on the solubility of cobalt.*

Amount of base added	Sodium hydroxide			Potassium hydroxide			Calcium oxide			Magnesium oxide			Ammonium hydroxide		
	pH	Concentration of cobalt	Relative amount of cobalt in solution	pH	Concentration of cobalt	Relative amount of cobalt in solution	pH	Concentration of cobalt	Relative amount of cobalt in solution	pH	Concentration of cobalt	Relative amount of cobalt in solution	pH	Concentration of cobalt	Relative amount of cobalt in solution
m.e.		Per cent	Per cent		Per cent	Per cent		Per cent	Per cent		Per cent	Per cent		Per cent	Per cent
0	0.95	2.358	100	1.10	2.358	100	1.25	2.358	100	1.02	2.358	100	1.10	2.358	100
4.70	5.75	2.358	100	2.75	2.358	100	2.27	2.358	100	2.40	2.358	100	6.38	2.358	100
4.90	6.42	2.34	99.5	6.56	2.30	97.7	4.62	2.30	97.7	3.40	2.30	97.7	6.60	2.358	100
7.14	6.60	2.20	93.5	6.56	2.13	90.5	6.57	2.24	95.1	6.40	2.18	92.6	6.57	2.22	94.3
10.70	6.63	2.00	85.0	6.67	1.98	84.0	6.57	2.00	85.0	6.46	1.94	82.3	6.59	1.91	81.2
16.05	6.61	1.60	68.0	6.72	1.41	59.6	6.60	1.65	70.0	6.54	1.64	69.5	6.75	1.57	66.9
20.07	6.67	1.44	61.0	6.80	1.19	50.7	6.63	1.46	62.0	6.59	1.49	63.2	6.87	1.45	61.4
26.75	6.81	0.85	36.0	7.04	1.03	43.8	6.74	1.00	42.5	6.71	1.02	43.3	7.13	0.986	41.1
32.10	7.04	0.53	22.5	7.25	0.595	25.2	6.85	0.70	29.7	6.82	0.55	23.3	7.35	0.682	29.0
37.50	7.47	0.188	8.0	7.70	0.214	9.1	7.13	0.38	16.2	7.15	0.22	9.35	7.46	0.56	23.8
42.80	8.55	0.0008**	0.03	8.13	0.0008**	0.03	8.88	0.0002**	0.008	8.66	0.0013**	0.005	8.13	0.29**	11.2
48.20	11.3	0**	0	12.2	0**	0	10.6	0**	0	8.95	0.0003**	0.001	8.60	0.37**	15.6

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* Ten ml. of 4 N cobaltous chloride in 0.48 N hydrochloric acid, treated with the indicated amounts of bases, were made up to 50 ml. and shaken 21 hours at 25° C ±1° C.

** Cobalt determined by Nitroso-R-salt method.

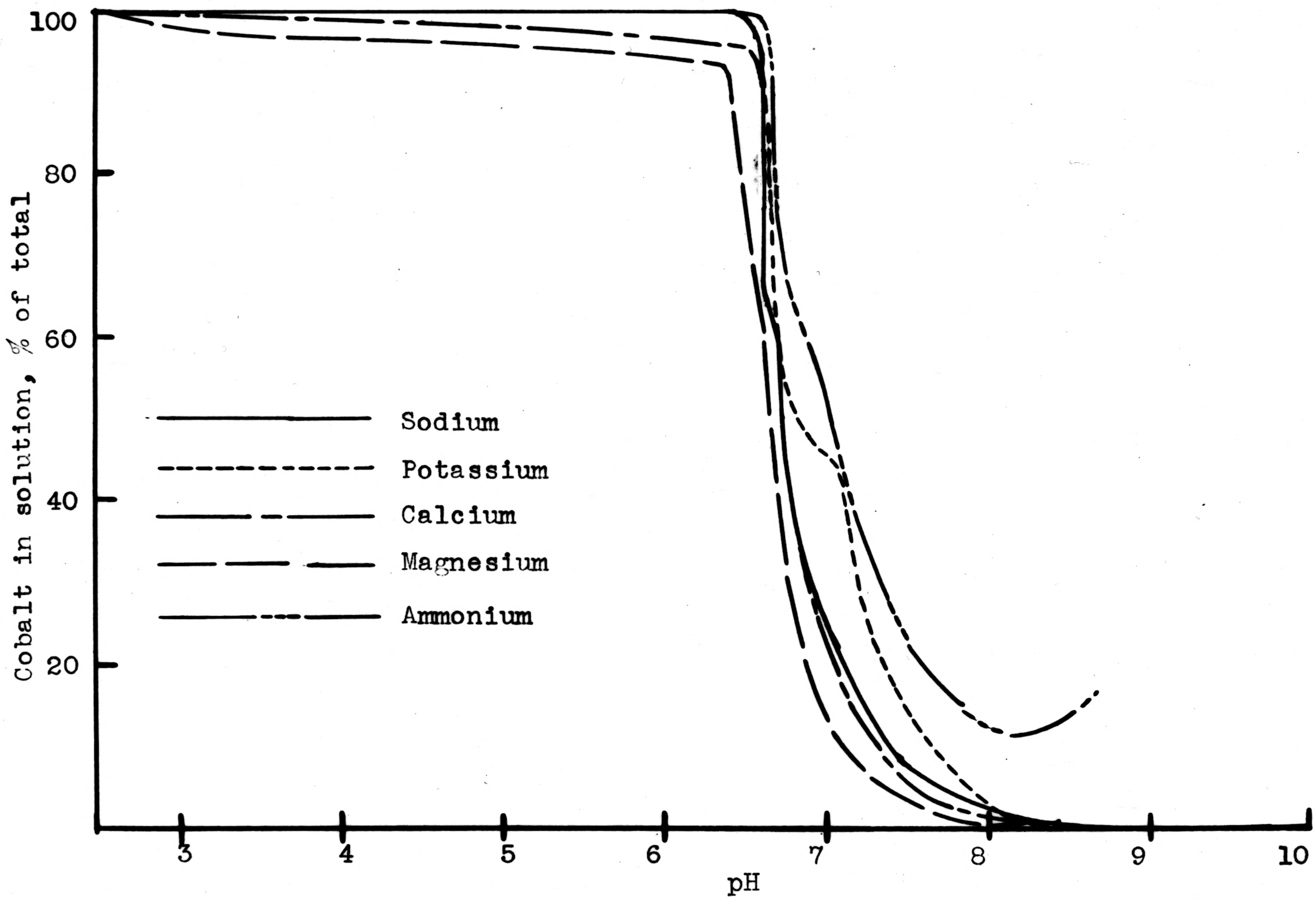

Fig. 5. Effect of hydrogen ion concentration and cations on the solubility of cobalt.

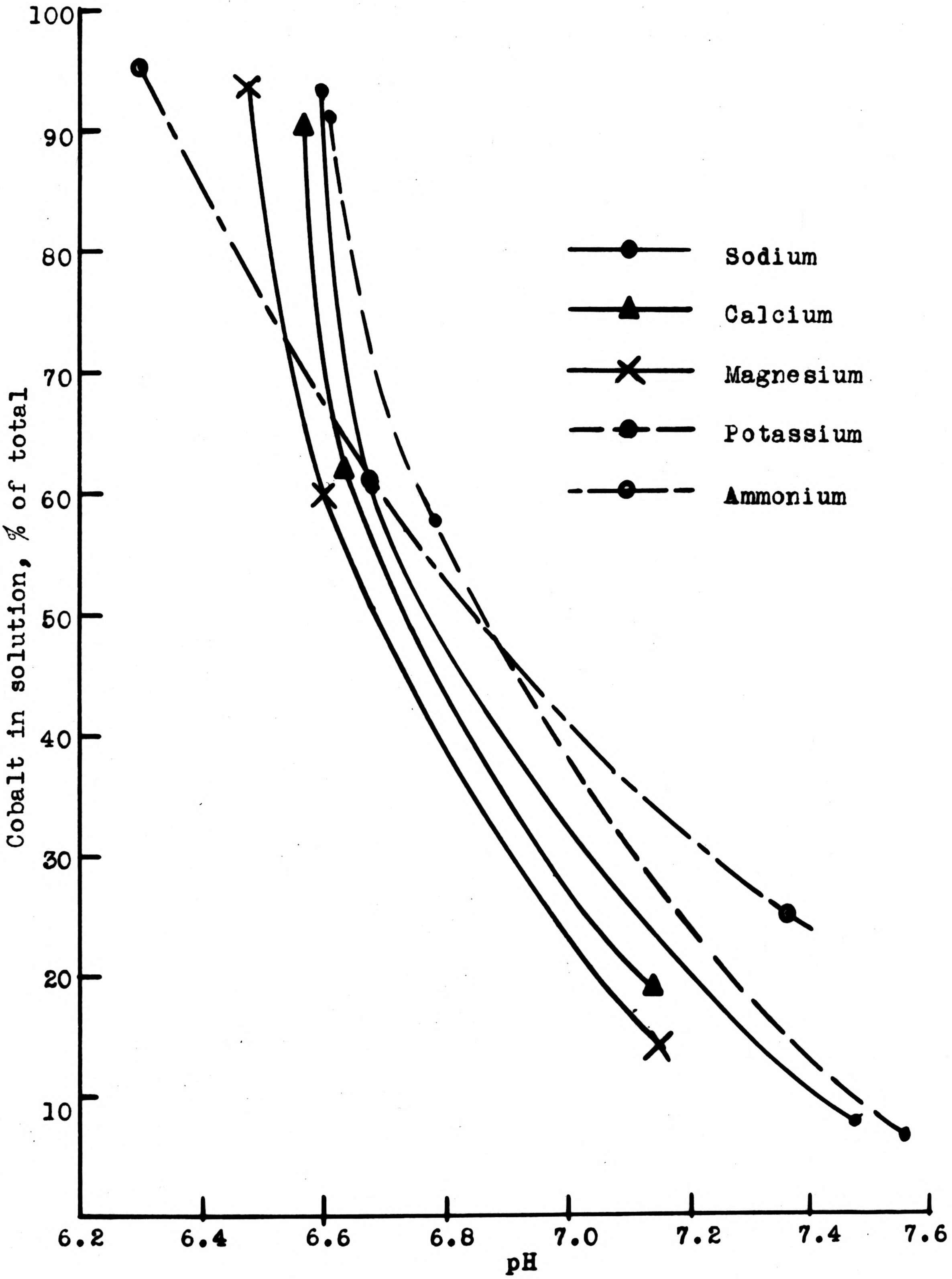

Fig. 6. Effect of hydrogen ion concentration and cations on the solubility of cobalt.

Table 8. The effect of hydrogen ion concentration and cations on the solubility of cobalt.*

Cation	Amount of cation added	pH	Cobalt concentration	Relative amount of cobalt in solution
	m.e.		Per cent	
Na	7.14	6.60	2.20	93.5
K	7.14	6.61	2.15	91.3
Ca	7.14	6.57	2.24	95.2
Mg	7.14	6.48	2.204	93.6
NH_4	7.14	6.30	2.24	95.2
Na	20.07	6.67	1.44	61.1
K	20.07	6.78	1.36	57.7
Ca	20.07	6.63	1.46	62.0
Mg	20.07	6.60	1.404	59.6
NH_4	20.07	6.68	1.432	60.8
Na	37.50	7.47	0.188	7.8
K	37.50	7.55	0.160	6.8
Ca	37.50	7.13	0.442	18.9
Mg	37.50	7.15	0.332	14.1
NH_4	37.50	7.36	0.584	24.8

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* (10 ml. of 4 N cobaltous chloride in 0.48 N hydrochloric acid with indicated amounts of bases were made up to 50 ml. and shaken 21 hours at 25° C. All manipulations were carried out simultaneously.)

When the hydrogen ion concentration was adjusted with sodium or potassium hydroxide, precipitation of cobalt began at about pH 6.6. Magnesium caused precipitation between pH 6.4 and 6.5, while calcium produced precipitation between pH 6.5 and 6.6. In one case a slight precipitate was obtained with ammonium ion at pH 6.3 and in another case was not obtained until near pH 6.6.

Above pH 8.0, potassium showed a greater ability to precipitate cobalt than the other ions did. At this point, the precipitate formed was very bulky and gelatinous. It may be possible that potassium does not cause precipitation of more cobalt than the other ions, but that the precipitate formed may include large quantities of cobalt still in solution, thus making it appear that precipitation is more complete. On the other hand, a different type of compound may be formed, and if this is the case, more cobalt may be tied up in its formation without a noticeable alteration of pH value.

When the pH was adjusted with ammonium hydroxide, the solubility of cobalt decreased to a pH value a little above 8.0 and then began to increase. This increase was probably due to the formation of a cobalt ammine which is water soluble.

The Effect of Hydrogen Ion Concentration and Anions on the Solubility of Cobalt

The data obtained from this phase of the experiment are shown in Tables 9 and 10. The data in Table 9 resulted from operations carried out on different days and hence may reflect the effects of uncontrolled variables such as those mentioned in the previous section. Those presented in Table 10, however, are the result of manipulations accomplished simultaneously and should be free from differences due to fluctuations in external conditions. The effect of the phosphate anion is omitted from Table 10 because, since cobaltous phosphate is not soluble enough to allow preparation of a solution with the same concentration as that used for the other ions, it was felt that a true comparison could not be obtained.

As was noted in the previous section (Fig. 5), cobaltous chloride began precipitating at about pH 6.6 when adjusted with sodium hydroxide. Precipitation was about 75 per cent complete at pH 7.0, and almost totally complete at pH 8.55.

Table 9. The effect of hydrogen ion concentration and anions on the solubility of cobalt.*

Cobaltous chloride				Cobaltous nitrate				Cobaltous sulfate				Cobaltous acetate				Cobaltous phosphate			
Amount of NaOH added	pH	Concentration of cobalt	Relative amount of cobalt in solution	Amount of NaOH added	pH	Concentration of cobalt	Relative amount of cobalt in solution	Amount of NaOH added	pH	Concentration of cobalt	Relative amount of cobalt in solution	Amount of NaOH added	pH	Concentration of cobalt	Relative amount of cobalt in solution	Amount of NaOH added	pH	Concentration of cobalt	Relative amount of cobalt in solution
m.e.		Per cent	Per cent	m.e.		Per cent	Per cent	m.e.		Per cent	Per cent	m.e.		Per cent	Per cent	m.e.		p.p.m.	Per cent
0	0.95	2.358	100.0	0	0.92	2.358	100.0	0	1.58	2.358	100.0	0	5.01	0.589	100.0	0	2.96	405**	100.0
4.7	5.75	2.358	100.0	4.76	2.30	2.358	100.0	4.14	3.15	2.358	100.0	4.60	6.24	0.589	100.0	0.55	4.78	200**	47.6
4.9	6.42	2.34	99.5	5.17	6.48	2.358	100.0	4.56	6.79	2.32	98.5	5.05	7.07	0.589	100.0	0.735	4.93	116**	27.6
7.14	6.60	2.20	93.5	7.14	6.80	2.27	96.5	7.14	6.97	2.14	91.2	7.23	7.32	0.563	90.7	1.470	6.10	8**	1.9
10.70	6.63	2.00	85.0	10.10	6.81	2.05	87.1	10.10	7.03	1.90	80.8	10.08	7.38	0.471	80.0	2.665	6.93	2.6**	0.62
16.05	6.61	1.60	68.0	16.35	6.89	1.62	68.7	16.35	7.09	1.47	62.5	16.43	7.54	0.272	46.2	3.676	7.90	0.6**	0.13
20.07	6.67	1.44	61.0	20.03	6.91	1.34	57.0	20.03	7.10	1.17	49.8	20.19	7.70	0.154	26.0	4.595	10.23	0.06**	0.013
26.75	6.81	0.85	36.0	27.10	7.00	0.96	40.7	27.10	7.28	0.67	28.5	27.20	8.27	0.016**	2.8	5.514	10.80	<0.06**	<0.013
32.10	7.04	0.53	22.5	32.70	7.09	0.63	26.8	32.70	7.48	0.28	11.8	32.60	11.45	0.00006**	0.001				
37.50	7.47	0.188	8.0	38.00	7.23	0.31	13.2	38.00	8.02	0.066	2.8	38.20	11.45	tr.**	--				
42.80	8.55	0.008**	0.03	43.50	7.65	0.05**	2.0	43.50	8.40	0.007**	0.5								
48.20	11.30	0**	0	48.90	11.2	0.0006**	0.003	48.90	11.20	0.0004**									

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* (10 ml. of 4 N cobaltous chloride, 10 ml. of 4 N cobaltous nitrate, 20 ml. of 2 N cobaltous sulfate, 20 ml. of 2N cobaltous acetate and 20 ml. of saturated solution of cobaltous phosphate in 0.2102 N phosphoric acid were treated with indicated amounts of sodium hydroxide, made up to 50 ml., shaken 21 hours at 25° C., filtered and analyzed for cobalt content).

** Cobalt determined by the Nitroso-R-salt method.

Table 10. The effect of hydrogen ion concentration and anions on the solubility of cobalt.*

Anion	Amount of NaOH added	pH	Cobalt concentration	Relative amount of cobalt in solution
	m.e.		Per cent	Per cent
Chloride	0	0.91	2.358	100.0
do	4.38	5.89	2.358	100.0
do	5.04	6.55	2.358	100.0
do	16.40	6.57	1.320	56.0
do	32.80	7.19	0.250	10.6
do	46.00	>11.00	0	0
Nitrate	0	0.89	2.358	100.0
do	4.16	1.93	2.358	100.0
do	5.04	6.65	2.304	98.0
do	20.80	6.91	1.260	53.5
do	32.80	7.24	0.406	17.2
do	46.00	>11.00	0	0
Sulfate	0	1.53	2.358	100.0
do	4.16	2.80	2.358	100.0
do	5.04	7.01	2.320	98.5
do	16.40	7.10	1.336	56.7
do	32.80	7.60	0.342	14.5
do	46.00	>11.00	0	0
Acetate	0	5.28	2.358	100.0
do	4.16	6.68	2.358	100.0
do	5.04	7.10	2.358	100.0
do	16.40	7.30	1.760	74.7
do	32.80	7.61	0.720	30.5
do	46.00	8.16	0.074	3.14

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* (10 ml. of 4 N cobaltous chloride and cobaltous nitrate and 20 ml. of 2 N cobaltous sulfate and cobaltous acetate were treated with the indicated amounts of NaOH, made up to 50 ml., shaken for 21 hours at 25° C., filtered and analyzed for cobalt content. All operations were accomplished simultaneously)

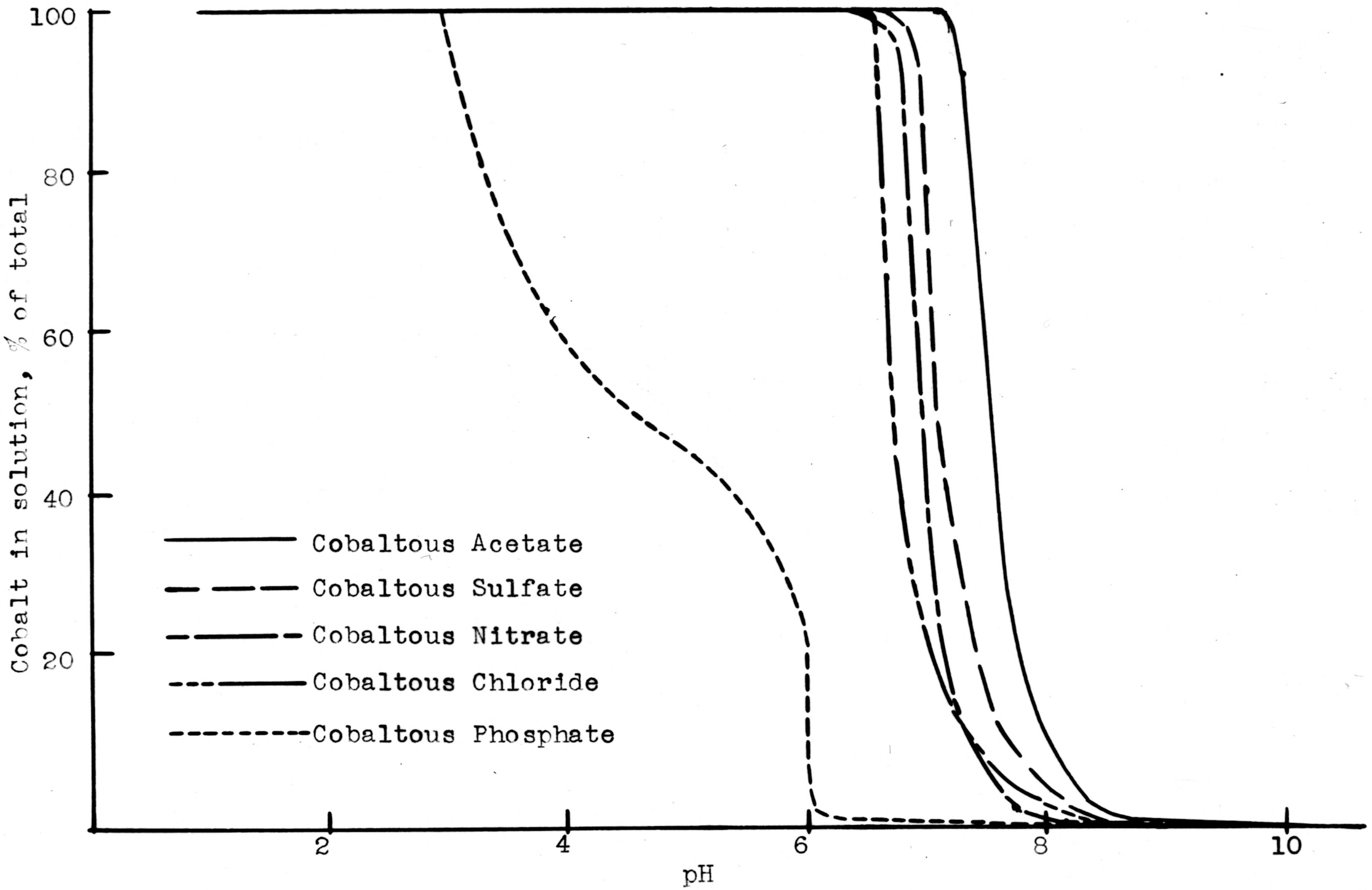

Fig. 7. Effect of hydrogen ion concentration and anions on the solubility of cobalt.

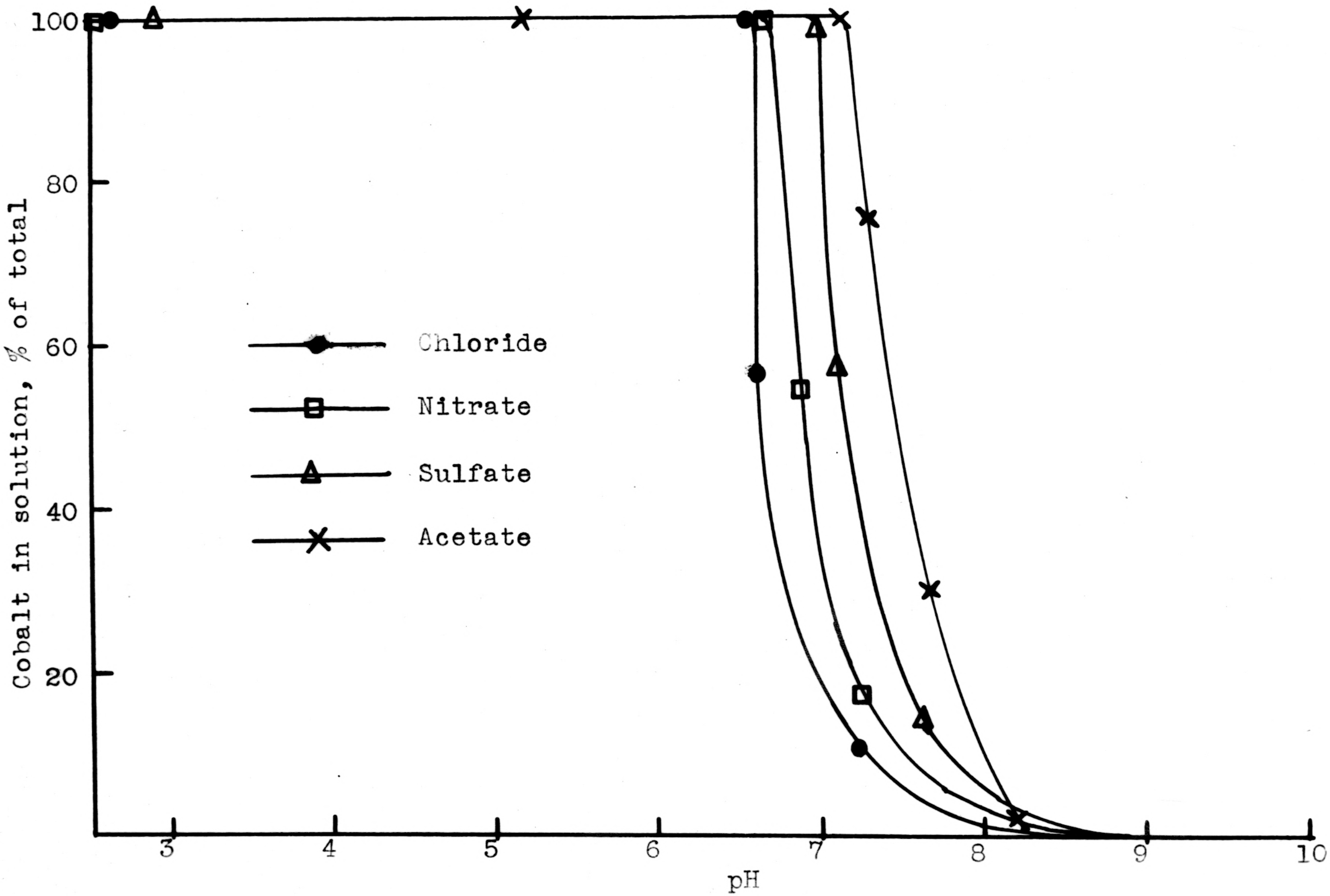

Fig. 8. Effect of hydrogen ion concentration and anions on the solubility of cobalt.

Cobaltous nitrate (Fig. 7) was very soluble up to about pH 6.8, above which point precipitation of cobalt proceeded very rapidly, being 60 per cent complete at pH 7.0, about 85 per cent complete at pH 7.2, and was completed somewhere above pH 8.5.

The same trend was followed with cobaltous sulfate (Fig. 7) except that precipitation of the cobalt did not begin with much rapidity until pH 7.0 was reached. At pH 7.1, 50 per cent of the cobalt was lost from solution and at a value somewhere above pH 8.5, precipitation was complete. The initial amount of cobalt in each of the above three solutions was 2.358 per cent.

Fig. 7 also shows that cobaltous acetate required more alkalinity for precipitation than the three previously discussed. No precipitation of cobalt occurred at pH 7.1, 90 per cent was still in solution at pH 7.3, about 10 per cent at pH 8.0 and only a trace at pH 11.4. The initial concentration of cobalt was 0.589 per cent.

Cobaltous phosphate is only sparingly soluble in water, but somewhat soluble in phosphoric acid. A saturated solution of cobaltous phosphate in 0.2102 N phosphoric acid in the amount of 20 ml. when diluted to 50 ml. resulted in a concentration of 0.0405 per cent or 405 p.p.m. cobalt. The pH of this solution was just below 3. Precipitation began immediately upon the addition of only minute quantities of sodium hydroxide. At pH 4.8 more than half of the cobalt originally in solution had precipitated and at pH 6.1 only 8 p.p.m. of cobalt remained in solution (Fig. 8). A possible explanation of this is that the cobalt in solution was in the form of $Co(H_2PO_4)_2$, which is somewhat soluble. An increase in pH resulted in its alteration to $CoHPO_4$, which was nearly insoluble, thus accounting for precipitation at such a low pH value. This was probably followed by the formation of $Co_3(PO_4)_2$ at higher pH values, which is nearly insoluble in water.

Fig. 8 shows the results obtained when solubilities of the chloride, nitrate, sulfate and acetate of cobalt at various pH values were determined at the same time under identical conditions. It merely substantiated the results already presented.

The Effect of Hydrogen Ion Concentration and Anions on the Extraction of Cobalt from Geary Silty Clay Loam

The data obtained from investigating the effect of hydrogen ion concentration and anions on the extraction of cobalt from soil are presented in Table 11. Total cobalt corresponded to 13 p.p.m. in the soil. No cobalt was extracted from Geary silty clay loam at pH 6.7 or 5.8 when 0.5 N solutions of the sodium salts of chlorine, nitrate, sulfate, acetate and phosphate were used as the extracting reagents. Half of these samples had 1.178 mgms. of cobalt added to 125 gms. of soil before extraction, and none of this was recovered. Approximately 0.5 N hydrochloric acid, nitric acid, and sulfuric acid extracted between 2.55 and 3.2 p.p.m. cobalt, while 0.5 N phosphoric acid extracted 0.4 p.p.m. and 0.49 N acetic acid extracted only a trace. This difference could not be attributed to a difference in the extracting ability of ions, but primarily to pH value. The first three acids had a pH below 1 and extracted far more than the others. Phosphoric acid with a pH of

Table 11. Effect of hydrogen ion concentration and anions on the extraction of cobalt from Geary silty clay loam.

Sample number	Extracting solution	pH of extract	Cobalt content of soil	pH of extract	Cobalt content of soil
			p.p.m.		p.p.m.
1	0.5 N. NaCl	6.7	0	5.8	0
2*	do	6.7	0	5.8	0
3	0.5N. $NaNO_3$	6.7	0	5.8	0
4*	do	6.7	0	5.8	0
5	0.5 N. Na_2SO_4	6.7	0	5.8	0
6*	do	6.7	0	5.8	0
7	0.5 N. $Na(CH_3COO)$	6.7	0	5.8	0
8*	do	6.7	0	5.8	0
9	0.5 N. Na_2HPO_4	6.7	0	5.8	0
10*	do	6.7	0	5.8	0
11	0.49 N. HNO_3	<1.0	2.55		
12	0.49 N. H_2SO_4	<1.0	3.20		
13	0.49 N. HCH_3COO	3.52	tr.		
14	0.50 N. H_3PO_4	2.13	0.40		
15	0.48 N. HCl	<1.0	2.80		
16	0.184 N. HCl	1.40	0.75		
17	0.092 N. HCl	2.13	0.38		
18	0.046 N. HCl	2.98	tr.		
19	0.0184 N. HCl	4.01	0		
20	0.0074 N. HCl	4.72	0		
21**	ignition + Con HCl	--	13.0		

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* 1.178 mgms. of cobalt were added to each 125 gms. of soil before extraction.

** Total cobalt.

2.13 extracted more than acetic acid with a pH of 3.52. When various concentrations of hydrochloric acid were used, the higher the pH value the less cobalt extracted until at pH 4, none was obtained. The results indicated that a pH value below 3.0 and 3.5 was necessary for the extraction of cobalt from Geary silty clay loam. No significant difference could be attributed to the various anions studied because the differences obtained were within the accuracy of the method used.

SUMMARY

The object of the experiment was to determine factors that might affect the solubility and availability of cobalt in soils. Factors studied were hydrogen ion concentration; the influence of cations, including sodium, potassium, calcium, magnesium, and ammonium; the influence of anions, including chloride, nitrate, sulfate, acetate and phosphate; and the effect of hydrogen ion concentration and anions on the extraction of cobalt from soil.

A colorimetric method for the rapid determination of cobalt in concentrated solutions of cobaltous salts is presented. Details of the Nitroso-R-salt method of determining cobalt in dilute solutions as recommended by Bayliss and Pickering with modifications made here are listed. In addition, a method of preparing soil extracts for analysis and for determining total cobalt in soils is given.

Data presented indicate that hydrogen ion concentration has a profound effect upon the solubility of cobalt. Cobalt is very soluble up to a certain pH value, depending on the anions present and to a lesser degree upon other cations. When this critical value is reached, the solubility decreases rapidly, approaching zero usually within 2 pH units, except where ammonium ion is present.

Precipitation of cobaltous chloride when magnesium oxide was used to adjust pH, started at a slightly lower value (pH 6.4 to 6.5) than calcium, which was lower than sodium and potassium (pH 6.60). These differences may not be significant and are not considered to be of much, if any, agricultural importance. The ammonium ion caused an increase in solubility of cobalt somewhere slightly above pH 8.1. It was suggested that this was due to the formation of a cobalt ammine, which is soluble.

Anions were found to exert a pronounced influence on the pH values at which cobalt precipitated when adjusted with sodium hydroxide. Cobaltous chloride began precipitating at about pH 6.6, cobaltous nitrate at about pH 6.8, cobaltous sulfate at about pH 7.0, cobaltous acetate at about pH 7.3, and cobaltous phosphate at about pH 3.0. Precipitation was nearing completion slightly above pH 8.5 in the case of the first four. The phosphate was 98 per cent precipitated at pH 6.1.

No cobalt was extracted from Geary silty clay loam at pH 5.8 or 6.7 when 0.5 N solutions of the sodium salts of chloride, nitrate, sulfate, acetate, and phosphate were used as extracting reagents, even when soluble cobalt was added to the soil before extraction. Approximately 0.5 N hydrochloric acid, nitric acid, and sulfuric acid extracted 2.8, 2.55, and 3.2 p.p.m. cobalt, respectively. The differences were within the accuracy of the method used and no conclusions were drawn as to the extracting ability of the three ions. Acetic acid (0.49 N) extracted a trace and 0.5 N phosphoric acid extracted 0.4 p.p.m. These lower values were attributed to their higher pH values (3.52 and 2.13 respectively) rather than any peculiarity of the acetate or phosphate ion. As the dilution and pH of hydrochloric acid increased, extraction of cobalt decreased until at pH 2.98, a trace was found and none at pH 4.01.

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LITERATURE CITED

(1) Ahmad, Bashir and E. V. McCollum.
Cobalt content of some food materials from different parts of the United States. Amer. Jour. Hyg. 29A:24-26. 1939.

(2) Askew, H. O.
Effect of pH value on solubility of cobalt phosphate. New Zeal. Jour. Sci. and Technol. 20A:106-109. 1938.

(3) Askew, H. O.
Cobalt deficiency at Glenhope, Nelson, New Zealand. New Zeal. Jour. Sci. and Technol. 20A:302-309. 1938.

(4) ――――――――
Animal tests with cobalt-containing limestones at Sherry River, Nelson, New Zealand. New Zeal. Jour. Sci. and Technol. 25A:154-160. 1943.

(5) Askew, H. O. and J. K. Dixon.
Influence of cobalt top dressing on cobalt status of pasture plants. New Zeal. Jour. Sci. and Technol. 18:688-693. 1937.

(6) Askew, H. O. and P. W. Maunsell.
The cobalt content of some Nelson pastures. New Zeal. Jour. Sci. and Technol. 19:337-342. 1937.

(7) Askew, H. O., T. Riggs, and D. J. Stanton.
Cobaltized superphosphate. New Zeal. Jour. Sci. and Technol. 20A:82-89. 1938.

(8) Becker, R. B., T. C. Erwin, and J. R. Henderson.
Relation of soil type and composition to the occurrence of nutritional anemia in cattle. Soil Sci. 62:383-392. 1946.

(9) Brenchley, W. E.
Comparative effect of cobalt, nickel, and copper on plant growth. Ann. Appl. Biol. 25:671-694. 1938.

(10) Carroll, Dorothy.
Mineralogy of some soils from Denmark, Western Australia. Soil Sci. 60:413-426. 1945.

(11) Corner, H. H. and Alexander M. Smith.
The influence of cobalt on pine disease in sheep. Biochem. Jour. 32:1800-1805. 1938.

(12) Filmer, J. F. and E. J. Underwood.
Enzootic Marasmus: Treatment with limonite fractions. Austral. Vet. Jour. 10:83-89. 1934.

(13) Geyer, R. P., I. W. Rupel, and E. B. Hart.
Cobalt deficiency in cattle in Northeastern Wisconsin. Jour. Dairy Sci. 28:291-296. 1945.

(14) Goldschmidt, V. M.
The geochemical background of minor element distribution. Soil Sci. 60:1-13. 1945.

(15) Harvey, R. J.
The Denmark wasting disease--cobalt status of some West Australian soils. West. Austral. Dept. Agr. Jour. 14:386-392. 1937.

(16) Kidson, E. B.
Cobalt status of New Zealand soils. New Zeal. Jour. Sci. and Technol. 18:694-707. 1937.

(17) __________
Some factors influencing the cobalt content of soils. Soc. Chem. Indus. Jour. 57:95-96. 1938.

(18) Kidson, E. B. and H. O. Askew.
A critical examination of the Nitroso-R-salt method for the determination of cobalt in pastures. New Zeal. Jour. Sci. and Technol. 21B:178-180. 1940.

(19) Killham, B. J.
Cobalt deficiency in some Michigan cattle. Amer. Vet. Med. Assoc. Jour. 99:279-282. 1941.

(20) Lyford, W. H. Jr., G. P. Percival, H. A. Keener, and K. S. Morrow.
The soils of New Hampshire as related to a deficiency in cattle responding to cobalt. Soil Sci. Soc. Amer. Proc. 10:375-380. 1946.

(21) McKnaught, K. J.
Cobalt content of limonites used in treatment of bush sickness. New Zeal. Jour. Sci. and Technol. 18:655-661. 1936.

(22) ______________
The cobalt content of North Island pastures. New Zeal. Jour. Sci. and Technol. 20A:14-30. 1938.

(23) ______________
A case of cobalt deficiency on a limestone soil. New Zeal. Jour. Sci. and Technol. 21A:343-44. 1939.

(24) McKnaught, K. J. and G. W. Paul.
Seasonal variation in cobalt content of North Island pastures. New Zeal. Jour. Sci. and Technol. 21B:95-100. 1939.

(25) Mellor, J. W.
A comprehensive treatise on inorganic and theoretical chemistry. New York, Longmans and Company, XIV:567, 586. 1935.

(26) Mitchell, R. L.
Distribution of trace elements in soil and grass. Proc. Nutrition Soc. (Eng. and Scot.) 1:183-189. 1944.

(27) ______________
Cobalt and nickel in soil and plants. Soil Sci. 60:63-70. 1945.

(28) Parks, R. Q., S. L. Hood, Charles Hurwitz, and G. H. Ellis.
Quantitative chemical microdetermination of twelve elements in plant tissue: A systematic procedure. Indus. and Engin. Chem., Analyt. Ed. 15:527-533. 1943.

(29) Patterson, J. B. E.
Cobalt and sheep diseases. Nature 140:363. 1937.

(30) Piper, C. S.
Soil and plant analysis. New York. Interscience Publishers, Inc. 367 p. 1944.

(31) Scharrer, K. and W. Schropp.
Sand and water culture experiments with nickel and cobalt. (From Chem. Abstracts, 27:5866. 1933.).

(32) Slater, C. S., R. S. Holmes, and H. G. Byers.
Trace elements in the soil from the erosion experiment stations with supplementary data on other soils. U. S. Dept. Agr. Tech. Bul. 552. 23 p. 1937.

(33) Stanton, D. J.
The cobalt content of some South Island (New Zealand) limestones. New Zeal. Jour. Sci. and Technol. 25A: 221-230. 1944.

(34) Stanton, D. J. and E. B. Kidson.
Cobalt status of soils and pasture in the Sherry and Wangapeka districts, Nelson. New Zeal. Jour. Sci. and Technol. 21B:65-76. 1939.

(35) Underwood, E. J. and J. F. Filmer
The determination of the biologically potent element, cobalt in limonite. Austral. Vet. Jour. 11:89-94. 1935.

(36) Willard, Hobart H. and Samuel Kaufman.
Colorimetric determination of cobalt using Nitroso-R-salt. Indus. and Engin. Chem., Analyt. Ed. 19:505. 1947.

(37) Young, R. S.
Rarer elements in soils and fertilizers. Cornell Univ. Agr. Expt. Sta. Memoir 174. 70 p. 1935.